



Employing supramolecular chemistry strategies for the separation of mixtures of anisole and bromoanisole isomers

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Abstract

In the present work, host compounds *trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate (**H1**), *trans*- α,α,α' , α' -tetraphenyl-9,10-dihydro-9,10-ethanoanthracene-11,12-dimethanol (**H2**) and *trans*- α,α,α' , α' -tetra(*p*-chlorophenyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dimethanol (**H3**) were assessed for their host ability for anisole (ANI) and 2-, 3- and 4-bromoanisole (2-, 3- and 4-BA). It was demonstrated that **H3** formed complexes with each of these guest species, while **H1** and **H2** only possessed the ability to enclathrate ANI. When **H3** was crystallized from equimolar binary guest solutions, a significantly enhanced host affinity was observed for ANI and 3-BA. As examples, equimolar binary ANI/2-BA and 2-BA/3-BA solutions afforded complexes that demonstrated a near-complete **H3** selectivity towards ANI (97.5%) and 3-BA (94.5%), respectively. Furthermore, from **H3** crystallization experiments in binary ANI/2-BA, ANI/4-BA, 3-BA/2-BA and 3-BA/4-BA mixtures, where the molar guest amounts were varied sequentially, were calculated significant selectivity coefficients (K values), so much so that **H3** may be used to separate very many of the guest anisole mixtures prepared in this work, through supramolecular chemistry strategies, which serves as a greener separation protocol compared with tedious and energy intensive fractional distillations. Thermal analyses were also used to investigate the relative stabilities of each of the single solvent complexes.

Keywords Host–guest · Bromoanisole · Anisole · Supramolecular chemistry · Separation

Introduction

Anisole (ANI) and the bromoanisole isomers (2-BA, 3-BA and 4-BA, Scheme 1) find important applications in perfumes, flavouring agents, pharmaceuticals and other organic synthesis procedures [1–5]. The BA isomers may be synthesized by means of the bromination of ANI, where a mixture of 2-BA and 4-BA usually results (together with a small quantity of 3-BA and, also, unreacted ANI) [6, 7]. These isomers may also be prepared by employing *O*-methylation procedures on the respective bromophenol starting compounds [8, 9]. Additionally, bromination of ANI can be achieved using *N*-bromophthalimide in the presence of

catalytic amounts of mercuric acetate with acetic acid as the solvent [10].

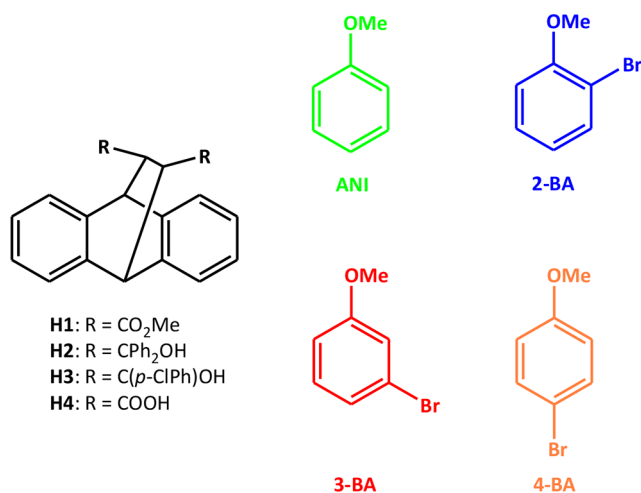
The boiling points of 2-BA, 3-BA and 4-BA are very similar (216, 211 and 223 °C, correspondingly) and, as a consequence, their separation by means of fractional distillation protocols is extremely challenging. Therefore, host–guest chemistry is an attractive alternative separation strategy for mixtures of these guest compounds.

The present work focusses on the roof-shaped compounds bearing the rigid 9,10-dihydro-9,10-ethanoanthracene framework, **H1–H3**, and investigates their host selectivity and thus their ability to serve as separatory tools for mixtures of 2-BA, 3-BA and 4-BA (for the sake of interest, ANI was also included in these investigations). These compounds were specifically selected as viable host candidates for these separations largely as a result of work carried out previously with the related host compound *trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (DED) (Scheme 1, **H4**) and these anisoles as guest species. In that investigation [11], DED was revealed to possess an extraordinary affinity for 4-BA (93.1–98.6%)

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Scheme 1 Molecular structures of host compounds **H1–H4** and the potential guest molecules ANI and 2-, 3- and 4-BA

during crystallization procedures from these guest solutions. Furthermore, remarkable results were obtained not only in binary guest mixtures, but also those ternary and even quaternary in nature. Moreover, host compounds **H1–H3** were shown in the recent past to also possess discriminatory behaviour in various mixtures such as ethylbenzene/xylenes [12, 13], dichlorobenzenes [14], anisole/methylanisoles [15] and pyridine/methylpyridines [16] and, in many instances, the observed host selectivities for one particular guest in these mixtures were significantly enhanced and, oftentimes, it was concluded that these mixtures may be separated by means of host–guest chemistry strategies when employing **H1–H3** as the applicable host compounds. This field of science offers a significantly greener separation protocol compared with other separatory methods since the host compound, after guest release, may be recycled and reused in the process.

We report now on the results so obtained and confirm that these have not been published on a prior occasion.

Materials and methods

General

All starting and guest materials were purchased from Sigma Aldrich, South Africa, and were used as received.

¹H-NMR experiments were carried out by means of a Bruker Ultrashield Plus 400 MHz spectrometer; CDCl₃ was the deuterated solvent.

Gas chromatographic experiments were carried out by means of an Agilent Technologies 7890 A gas chromatograph equipped with an Agilent 5975 C VL mass spectrometer. An Agilent J&W Cyclosil-B column served

as the stationary phase with helium gas being the mobile phase. The split ratio was 80:1. The metal plates of the inlet and detector were maintained at 220 and 300 °C, respectively. The column was initially heated and maintained at 50 °C. The first heating ramp of 15 °C·min⁻¹ then raised the column temperature to 150 °C. A second heating ramp (20 °C·min⁻¹) allowed the final column temperature to reach 170 °C (which was maintained for 1 min). The flow rate varied between 1 and 1.3 mL·min⁻¹. Dependent upon availability, a Young Lin YL6500 gas chromatograph coupled to a flame ionization detector was also employed. The column was as before, while both hydrogen gas (30 mL·min⁻¹) and air (300 mL·min⁻¹) served as the mobile phase. The split ratio was, once more, 80:1. The inlet and detector metal plates were maintained at 200 and 300 °C, respectively. The column was heated from 50 °C to 200 °C by implementing a heating ramp of 20 °C·min⁻¹. This final temperature was held for 1 min, and the final run time was 8.5 min. The flow rate was 2 mL·min⁻¹. Finally, in all GC experiments, dichloromethane served as the dissolution solvent.

The single solvent complexes for the thermal experiments were recovered from the glass vials by means of suction filtration, washed with petroleum ether (bp 40–60 °C) and analysed without further manipulation. The appropriate instrument was a TA SDT Q600 Module system; data were analysed using TA Universal Analysis 2000 software. Samples were placed in open ceramic pans whilst an empty pan served as the reference. The purge gas was high purity nitrogen, and the samples were heated from 40 to 400 °C at a heating rate of 10 °C·min⁻¹.

Synthesis of host compounds H1, H2 and H3

Host compounds **H1–H3** were prepared by considering previous literature reports [17–19].

Crystallization experiments of H1–H3 from ANI and 2-, 3- and 4-BA

It was required at the outset to determine whether host compounds **H1–H3** possess host ability for each of ANI and 2-, 3- and 4-BA. To this end, the host compound was dissolved in an excess of each of these anisoles in glass vials which were subsequently left open to the ambient conditions. In this fashion, some solvent evaporated off and crystallization proceeded. (**H1** and **H2** required three to four months for crystallization to occur (if this occurred at all), while **H3** crystallized rapidly, within one or two days.) The crystals were collected by suction filtration, washed with petroleum ether (bp 40–60 °C) and then analysed by means of ¹H-NMR spectroscopy. This technique revealed whether complexation had been successful, in which instance the

host: guest (H: G) ratio was calculated from the resultant spectra by considering the areas under the peaks of appropriate host and guest resonance signals.

Crystallization experiments of H3 from equimolar mixtures of ANI and 2-, 3- and 4-BA

Owing to the successful complexation of each of the guest anisoles using **H3** as the host compound, an investigation of its host selectivity when presented with guest mixtures was subsequently undertaken. (Note that only the behaviour of **H3** was investigated in mixed guests owing to its rapid crystallization from these solutions (one to two days) and the prolonged crystallization times (three to four months) required for **H1** and **H2** to form crystals and also since the single solvent experiments with these two host compounds mostly resulted in gels (no crystallization occurred).) Therefore, **H3** (0.04 g) was dissolved in every combination of equimolar guest mixtures (combined amount 5 mmol) in glass vials. These were closed and stored at 4 °C. The crystals that formed in this way were treated as in the single solvent experiments, and analysis was then by means of ¹H-NMR spectroscopy (to obtain the overall H: G ratios) and GC (to quantify the guest compounds in any mixed complexes that formed).

Crystallization of H3 from binary guest mixtures in which the molar amounts of each guest species was varied sequentially.

The host selectivity behaviour of **H3** was also assessed in binary guest anisole mixtures (G_A and G_B) in which the molar amount of each guest was varied sequentially; applicable $G_A:G_B$ molar ratios ranged between 80:20 and 20:80 mol%. (Once more, only **H3** was investigated in these conditions for the reasons already described above.) This host species was crystallized from these binary guest solutions according to the method described for the experiments that employed equimolar guest mixtures (host and combined guest amounts also remained unchanged). Both the crystals that formed and the solution from which these formed were analysed by means of GC. A plot of the molar ratio of G_A

(or G_B) in the crystals (Z) against G_A (or G_B) in the solution (X) therefore afforded selectivity plots which demonstrated how the selectivity behaviour of the host compound changed when the $G_A:G_B$ molar ratios were varied. In order to measure this selectivity, the selectivity coefficient (K) was calculated in each instance by employing the equation $K_{A:B} = Z_A/Z_B \times X_B/X_A$, where $X_A + X_B = 1$ [20]. $K = 1$ represents an unselective host compound and this circumstance is represented by the straight-line diagonal plots that have been inserted into each of these selectivity profiles for facile comparison purposes with the experimentally obtained data points.

Results and discussion

Crystallization experiments of H1–H3 from ANI and 2-, 3- and 4-BA

Table 1 contains the H: G ratios of complexes formed in the single solvent crystallization experiments of **H1–H3** from ANI, 2-BA, 3-BA and 4-BA, as obtained from ¹H-NMR experiments.

Table 1 shows that attempts to crystallize **H1** and **H2** from 2-BA, 3-BA and 4-BA were unsuccessful, and gels remained in the glass vials. However, both **H1** and **H2** enclathrated ANI, forming 3:1 H: G complexes with this guest in both instances. In contrast, **H3** successfully included all four guest compounds, with ratios of 1:1 (ANI and 3-BA), 2:1 (2-BA) and 1:2 (4-BA).

Due to the prolonged time required for **H1** and **H2** to form complexes with ANI and the emergence of gels in the remaining experiments, these host compounds were excluded from further investigation. **H3**, on the other hand, was subjected to further scrutiny due to its capability of forming complexes with each of the four guest compounds within a two-day timeframe.

Crystallization experiments of H3 from equimolar mixtures of ANI and 2-, 3- and 4-BA

The H: G and G: G ratios resulting from the equimolar binary, ternary and quaternary ANI and BA guest mixtures are presented in Table 2 after **H3** was crystallized from these mixtures. The preferred guests in each of these guest competition experiments are indicated in red bold font face, and the percentage estimated standard deviations (%e.s.d.s) are provided in parentheses as a result of the experiments

Table 1 The H: G ratios of complexes of **H1–H3** when crystallized from ANI and the BA isomers

Guest	H1	H2	H3
ANI	3:1	3:1	1:1 ^a
2-BA	<i>b</i>	<i>b</i>	2:1
3-BA	<i>b</i>	<i>b</i>	1:1
4-BA	<i>b</i>	<i>b</i>	1:2

^aThe complex with ANI has been reported on an earlier and unrelated occasion [15]

^bCrystallization failed and a gel remained in the glass vessel

Table 2 The overall H: G and G: G ratios of complexes of **H3** when crystallized from equimolar ANI and BA mixtures^{a,b}

ANI	2-BA	3-BA	4-BA	Guest ratios (%e.s.d.s)	Overall H: G ratio
X	X			97.5:2.5 ^c	1:1
X		X		67.5:32.5 ^c	1:1
X			X	90.7:9.3 ^c	1:1
	X	X		5.5:94.5 (0.9)	1:1
	X		X	^d	–
		X	X	90.4:9.6 (0.7)	1:1
X	X	X		39.5:3.0:57.5 (1.3)(0.1)	1:1
			X	(1.2)	
X	X		X	84.1:4.6:11.3 (0.2)(0.1)	1:1
			X	(0.1)	
X		X	X	33.6:60.0:6.4 (0.4)(0.3)	1:1
			X	(0.1)	
	X	X	X	2.1:93.9:4.0 (0.5)(1.4)	1:1
			X	(0.9)	
X	X	X	X	37.5:1.6:57.1:3.8 (2.2)	1:1
			X	(0.1)(2.0)(0.3)	

^aOverall H: G and G: G ratios were obtained using ¹H-NMR spectroscopy and GC analyses, respectively.

^bThe experiments were conducted in duplicate and %e.s.d.s are provided in parentheses.

^cThe %e.s.d. could not be determined due to the presence of only a singular data point; the duplicate experiment did not crystallize

^dA gel remained in the vial, and no crystals formed.

being carried out in duplicate, where possible, as evidence of replicability.

Host compound **H3** possessed selectivity for ANI in the binary crystallization experiments; this selectivity was near-complete (97.5%, in favour of ANI) in the ANI/2-BA experiment, and this preferential behaviour for ANI persisted in the ANI/3-BA (67.5%) and ANI/4-BA (90.7%) experiments. In the absence of ANI, 3-BA was then favoured in these binary mixtures; once more, the selectivity behaviour of **H3** was near-complete for this guest compound in both instances (94.5% in 2-BA/3-BA and 90.4% in 3-BA/4-BA).

In the ternary and quaternary experiments, 3-BA emerged as the preferred guest, yielding crystals with up to 93.9% 3-BA in the 2-BA/3-BA/4-BA experiment. However, **H3** crystallized with only moderate amounts of 3-BA in competition experiments with solutions ANI/2-BA/3-BA (57.5%), ANI/3-BA/4-BA (60.0%) and ANI/2-BA/3-BA/4-BA (57.1%). The addition of ANI to the 2-BA/4-BA experiment (ANI/2-BA/4-BA) produced a solid with up to 84.1% ANI. The overall H: G ratio remained 1:1 for all experiments (except in the 2-BA/4-BA experiment which did not crystallize), consistent with the ratios observed in the single solvent experiments with the preferred ANI and 3-BA guests (1:1 H: G ratio in each instance).

Unfortunately, therefore, **H3** proved to be an unlikely host candidate for the separation of 2-BA/4-BA mixtures, but it proved to be an extremely capable host candidate for isolating ANI and 3-BA from various equimolar binary and ternary mixtures of these guest compounds.

Crystallization of **H3** from binary guest mixtures in which the molar amounts of each guest species was varied sequentially.

Five selectivity profiles (Fig. 1a–e) for the binary guest experiments with **H3** were constructed by plotting Z_A (or Z_B) against X_A (or X_B). Note that the 2-BA/4-BA selectivity profile could not be obtained here since these solutions furnished gels with the host compound, and crystallization was not successful.

From these figures, it is evident that **H3** was selective for either ANI (in ANI/2-BA and ANI/4-BA mixtures) (Fig. 1a and c) or 3-BA (in the 3-BA/2-BA and 3-BA/4-BA experiments) (Fig. 1d and e) across the concentration range. Nasimbeni and coworkers reported that, for feasible separation processes on an industrial platform, K values are required to be equal to or greater than 10 [21]. Therefore, due to the high selectivity coefficients calculated in the ANI/4-BA (Fig. 1c, $K_{ave} = 17.8$), 3-BA/2-BA (Fig. 1d, $K_{ave} = 18.7$) and 3-BA/4-BA (Fig. 1e, $K_{ave} = 21.5$) experiments (where K_{ave} is the average of the K values obtained for each data point in a set of data points), **H3** may be considered for applications in the separation and isolation of either ANI or 3-BA from these mixtures. Furthermore, the host selectivity for ANI in ANI/2-BA mixtures, where the concentration of ANI was 40% or greater, was also extremely high (Fig. 1a): for example, the complex contained 95.9% ANI when the solution comprised only 41.0% of this guest solvent (K , here, was 34.0, and hence this separation would also be a feasible one). However, the selectivity of **H3** was guest concentration-dependent when presented with ANI/3BA mixtures (Fig. 1b) (ANI was only favoured when the solution contained more than 50% ANI), and K values were low in these experiments (1.4–3.2).

In summary, **H3** displayed a significant ability for the separation and isolation of either ANI from ANI/2-BA and ANI/4-BA mixtures or 3-BA from 3-BA/2-BA and 3-BA/4-BA mixtures.

Regrettably, SCXRD analyses were not possible on any of the **H3** complexes with these anisoles owing to poor crystal quality, with the exception of the ANI-containing complex, which has been reported on an earlier and unrelated occasion [15]. (Note that the apohost (guest-free) crystal structure for **H1** has been reported [22], while these for **H2** and **H3** could not be isolated without the presence of a guest species.)

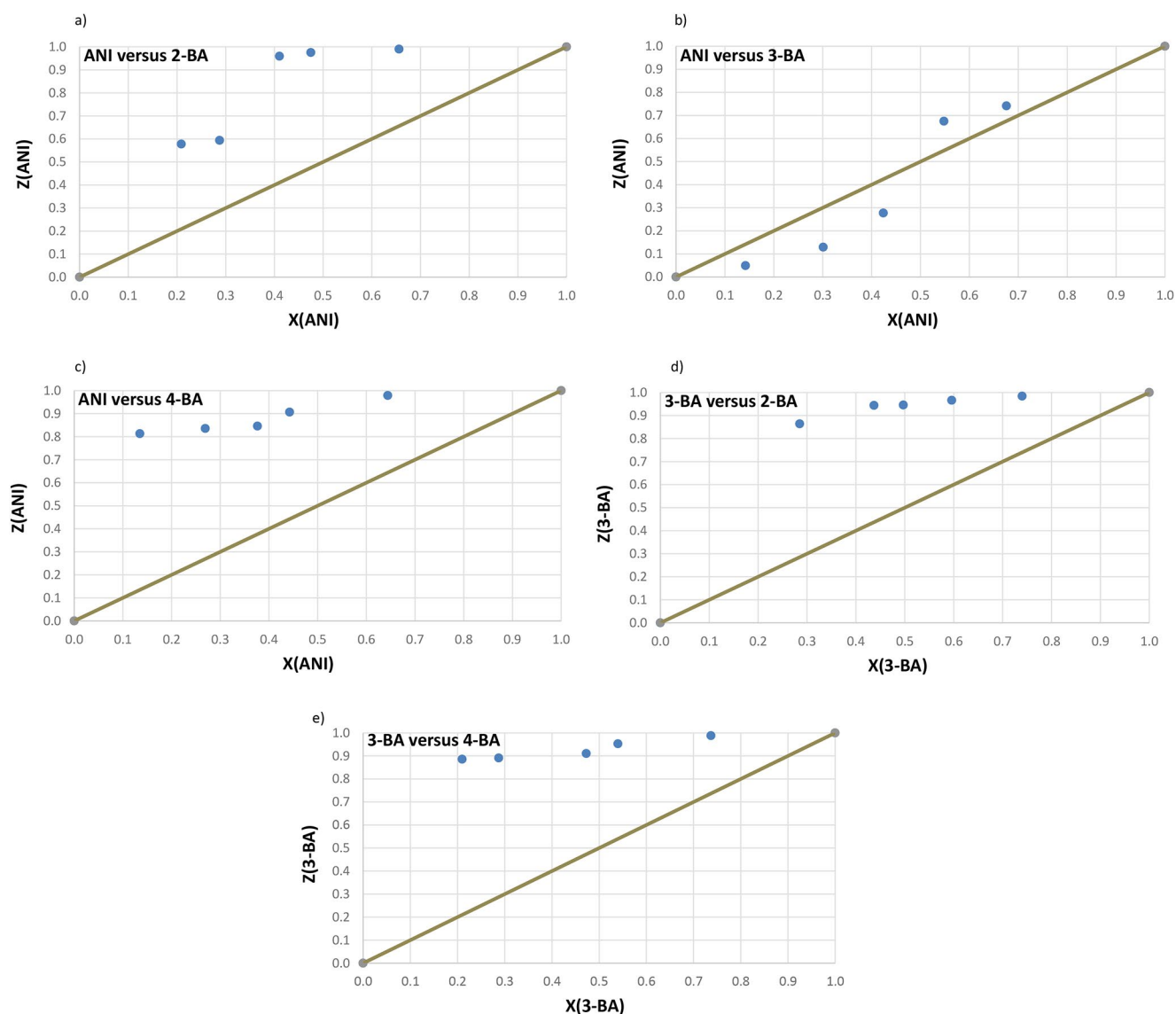


Fig. 1 Selectivity profiles of **H3** when presented with the **a)** ANI/2-BA, **b)** ANI/3-BA, **c)** ANI/4-BA, **d)** 3-BA/2-BA and **e)** 3-BA/4-BA binary mixtures

Thermal analyses

Table 3 contains the thermal data for the four anisole complexes with **H3** after heating these from approximately 40 to 400 °C at a rate of 10 °C·min⁻¹. The resulting thermogravimetric (TG), its derivative (DTG) and the differential scanning calorimetric (DSC) traces are provided in Fig. 2a–c for the inclusion compounds with 2-, 3- and 4-BA (these thermograms and associated data for the ANI-containing complex were reported on a prior occasion [15]).

From Table 2, the more thermally stable complexes (with the greater T_{on} values) were those containing the less favoured 2-BA and 4-BA guests (T_{on} 167.7 and 167.0 °C, respectively), while the favoured ANI and 3-BA guests were released at lower temperatures (94.7 and 139.1 °C).

Therefore, curiously, the complexes with the more favoured guest species possessed lower thermal stabilities than the complexes with guests less preferred. The measured and expected mass losses of each of the complexes with 2-BA, 3-BA and 4-BA could not be measured since the guest release process ultimately coincided with the host melt/decomposition event. Unfortunately, therefore, these thermal experiments do not wholly explain the selectivity of **H3** for ANI and 3-BA.

Table 3 Thermal data for the **H3**·ANI, **2(H3)**·2-BA, **H3**·3-BA and **H3**·2(4-BA) complexes

Complex	T _{on} ^a /°C	T _p ^a /°C	Measured mass loss /%	Expected mass loss /%
H3 ·ANI ^b	94.7	179.3, 209.0	12.2	13.2
2(H3) ·2-BA	167.7	221.3, 246.8, 267.1	^c	11.7
H3 ·3-BA	139.1	183.1	15.4 ^c	20.9
H3 ·2(4-BA)	167.0	201.9, 258.8	^c	34.6

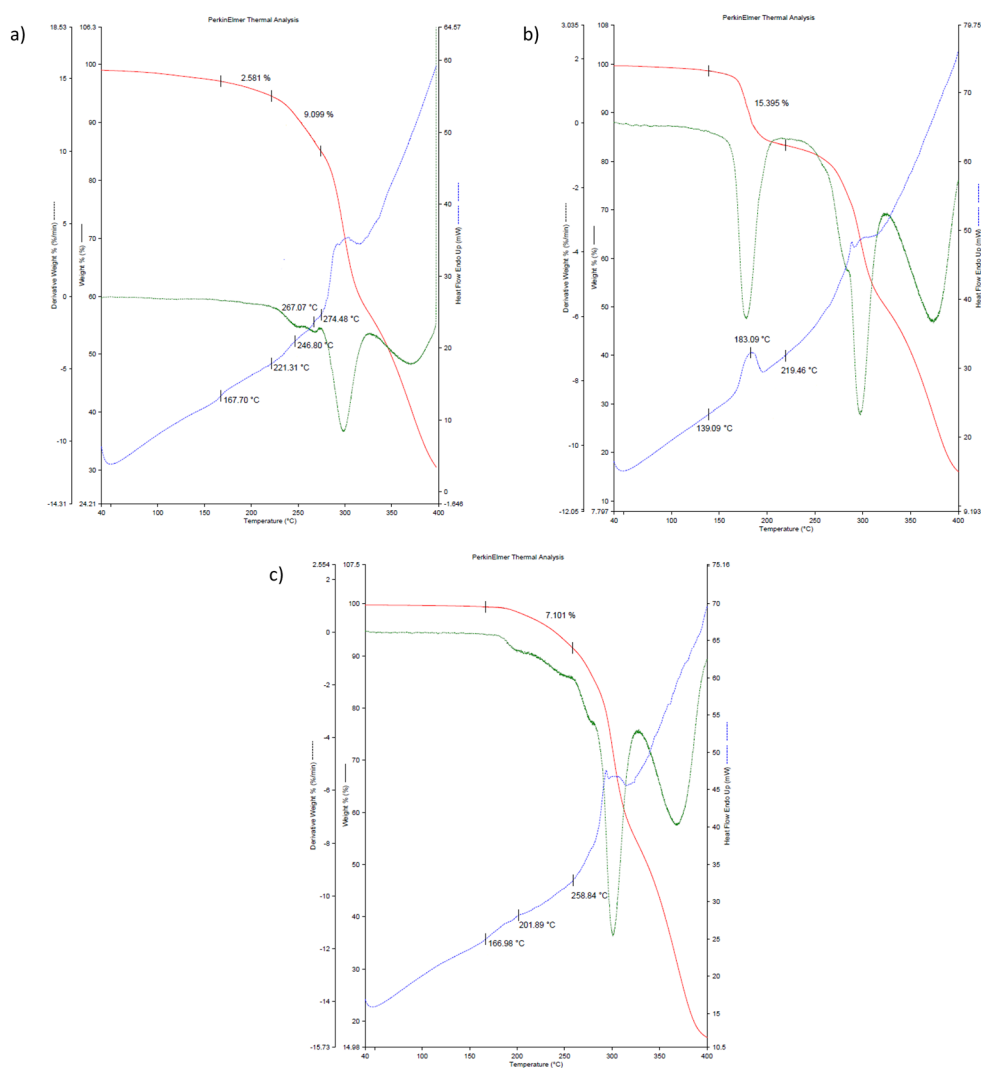
^aT_{on} is the onset temperature at which guest release was initiated and serves as a measure of the relative thermal stability of a complex, while T_p refers to the peak temperature of the guest release process as per the DTG trace

^bThermal data of this complex were reported before [15]

^cGuest release and host melt/decomposition were ultimately concomitant

Conclusions

Fig. 2 The DSC (blue), TG (red) and DTG (green) traces for **a** **2(H3)**·2-BA, **b** **H3**·3-BA and **c** **H3**·2(4-BA) (these traces for the ANI-containing complex have been published before [15])



Here, **H3** was demonstrated to have the ability to form complexes with each of the anisole and bromoanisole guests, forming either 1:1 (ANI and 3-BA), 2:1 (2-BA) or 1:2 (4-BA) H: G complexes. **H3** displayed a significant preference for both ANI and 3-BA as is evident from the equimolar binary guest competition experiments, where as much as 97.5% ANI (ANI/2-BA) and 94.5% 3-BA (2-BA/3-BA) were enclathrated. The equimolar quaternary guest mixture resulted in crystals containing only moderate amounts of both ANI (37.5%) and 3-BA (57.1%). Furthermore, this host compound also showed a remarkable affinity for either ANI or 3-BA in binary experiments where the molar amount of each guest present was varied. Here, **H3** was able to selectively include either ANI or 3-BA in ANI/2-BA, ANI/4-BA, 3-BA/2-BA or 3-BA/4-BA mixtures; however, in the ANI/3-BA experiments, host selectivities were low. From many of these binary guest solvent experiments was calculated significant K values, alluding to the feasibility of using **H3** for their separation, a greener separation methodology compared with tedious and energy intensive

fractional distillations. Unfortunately, single crystal X-ray diffraction analyses were not possible on complexes with the bromoanisoles as a result of poor crystal quality. Finally, the relative thermal stabilities of the complexes from thermal analyses did not wholly explain the host selectivity of **H3** for ANI and 3-BA.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10847-024-01242-4>.

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Author contributions B.B. and U.S. wrote the main manuscript text; Ulrich Senekal prepared all of the figures.

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Data availability No datasets were generated or analysed during the current study.

Declarations

Ethical approval This was not a requirement; the work involved no animals or human beings;

Consent to participate Both authors agreed to participate in this work;

Consent for publication Both authors have given their consent for publication.

Competing interests The authors declare no competing interests.

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References

- Dang, D., Wang, Z., Lin, W., Song, W.: Synthesis of anisole by vapor phase methylation of phenol with methanol over catalysts supported on activated alumina. *Chin. J. Catal.* **37**, 720–726 (2016)
- Zilberman, J.: One-step preparation of some 3-substituted anisoles. *Org. Process. Res. Dev.* **7**, 303–305 (2003)
- Nasipuri, D., Mitra, A.K.: Synthetic studies in the diterpene series. Part VIII. Synthesis of miltirone, a diterpenoid quinone. *J. Chem. Soc. Perkin Trans. 1*, 285–287 (1973)
- Protiva, M.: Moxifetin hydrogen maleate. *Drugs Future.* **16**, 911–916 (1991)
- Ramalingam, S., Periandy, S.: Spectroscopic investigation, computed IR intensity, Raman activity and vibrational frequency analysis on 3-bromoanisole using HF and DFT (LSDA/MPW1PW91) calculations. *Spectrochim Acta Part. A.* **78**, 835–843 (2011)
- Gupta, A.K., Gupta, B.: Mechanism of organic reactions: For world of competitions, Ajnish Academy.: India (2020)
- Smith, M.B., Organic synthesis: Elsevier.: (2016). United States
- Bidleman, T.F., Brorström-Lundén, E., Hansson, K., Laudon, H., Nygren, O., Tysklind, M.: Atmospheric transport and deposition of bromoanisoles along a temperate to arctic gradient. *Environ. Sci. Technol.* **51**, 10974–10982 (2017)
- Tundo, P., Andraos, J.: Green Synthesis. CRC, Boca Raton (2014)
- Anjaiah, B., Satish Kumar, M.S., Srinivas, P., Rajanna, K.C.: Bromination of anisoles using *N*-bromophthalimide: A synthetic and kinetic approach. *Int. J. Chem. Kinet.* **48**, 98–105 (2015)
- Barton, B., Caira, M.R., Senekal, U., Hosten, E.C.: *trans*-9,10-Dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid: Remarkable host selectivities in the presence of mixtures of anisole and bromoanisole isomers. *Cryst. Growth Des.* **23**, 501–510 (2023)
- Barton, B., Senekal, U., Hosten, E.C.: Comparing the host behaviour of roof-shaped compounds *trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid and its dimethyl ester in the presence of mixtures of xylene and ethylbenzene guests. *CrystEngComm.* **23**, 4560–4572 (2021)
- Barton, B., Senekal, U., Hosten, E.C.: *trans*- $\alpha,\alpha,\alpha',\alpha'$ -Tetraphenyl-9,10-dihydro-9,10-ethanoanthracene-11,12-dimethanol and its tetra(*p*-chlorophenyl) derivative: Roof-shaped host compounds for the purification of aromatic C₈H₁₀ isomeric guest mixtures. *J. Incl. Phenom. Macrocycl. Chem.* **102**, 77–87 (2022)
- Barton, B., Caira, M.R., Senekal, U., Hosten, E.C.: Host compounds based on the rigid 9,10-dihydro-9,10-ethanoanthracene framework: Selectivity behaviour in mixed isomeric dichlorobenzenes. *CrystEngComm.* (2024). <https://doi.org/10.1039/d4ce00113c>
- Barton, B., Caira, M.R., Senekal, U., Hosten, E.C.: Selectivity considerations of roof-shaped host compound *trans*- $\alpha,\alpha,\alpha',\alpha'$ -tetrakis(4-chlorophenyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dimethanol in mixed anisoles. *Cryst. Growth Des.* **22**, 6818–6827 (2022)
- Barton, B., Caira, M.R., Senekal, U., Hosten, E.C.: Complementary host behaviour of three anthracenyl-derived roof-shaped compounds in mixed pyridines. *CrystEngComm.* **25**, 1740–1754 (2023)
- Weber, E., Hens, T., Gallardo, O., Csöreg, I.: Roof-shaped hydroxy hosts: Synthesis, complex formation and X-ray crystal structures of inclusion compounds with EtOH, nitroethane and benzene. *J. Chem. Soc. Perkin Trans. 2*, 737–745 (1996)
- Bachmann, W.E., Scott, L.B.: The reaction of anthracene with maleic and fumaric acid and their derivatives and with citraconic anhydride and mesaconic acid. *J. Am. Chem. Soc.* **70**, 1458–1461 (1948)
- Yates, P., Eaton, P.: Acceleration of the diels-Alder reaction by aluminium chloride. *J. Am. Chem. Soc.* **82**, 4436–4437 (1960)
- Pivovar, A.M., Holma, K.T., Ward, M.D.: Shape-selective separation of molecular isomers with tunable hydrogen-bonded host frameworks. *Chem. Mater.* **13**, 3018–3031 (2001)
- Sykes, N.M., Su, H., Weber, E., Bourne, S.A., Nassimbeni, L.R.: Selective enclathration of methyl- and dimethylpiperidines by fluorenol hosts. *Cryst. Growth Des.* **17**, 819–826 (2017)
- Senekal, U.: Investigation of four roof-shaped host compounds for their separation potential of mixtures of guest isomers and

related compounds. PhD Thesis. Nelson Mandela University
(2024)

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